



STM Movies: Water in Motion

Atomic Scale Dynamics and Clustering Revealed

As reported in the September 13, 2002 issue of *Science*, a team led by Miquel Salmeron has imaged the motion of individual water molecules adsorbed on a single crystal metal surface. At 40 K to 60 K, temperatures at which molecular motion is slowed, the researchers observed collisions and the formation of dimers, trimers, tetramers and pentamers of H-bonded water molecules. "Movies" of images acquired at ~20 second intervals offered unprecedented insights into this diffusion and aggregation behavior. It was found, for example, that the dimers, trimers, and tetramers diffuse much faster than single molecules, while clusters containing 5 or more molecules diffuse more slowly or not at all.

Important phenomena such as wetting, corrosion, ice melting, electrochemistry, dissolution, and solvation are driven by the properties of water at the molecular level, with the water in contact either with itself or with other molecules or surfaces. Despite this widespread importance, numerous fundamental questions regarding the adsorption of water on surfaces and the aggregation of isolated molecules to form clusters, complete layers, and beyond remain unanswered. Clusters have been analyzed by several groups using vibrational spectroscopy techniques, but these are not ideal tools, as shown by the discrepancies in vibrational mode assignments reported by the different groups. In addition, these are primarily structural probes and do not address the important issue of the movement of water on surfaces. Further, these techniques involve the averaging of the motion of a large number of molecules, and cannot provide details of aggregation of individual molecules, or of the existence of cooperative phenomena. For this, the imaging of individual atoms or molecules is required. This has not been done until today except for the case of a limited number of metallic elements using the field ion microscope.

The Berkeley Lab team used the atomic resolution capability of scanning tunneling microscopy (STM) to, for the first time, obtain detailed information on the structure and dynamics of individual adsorbed water molecules. The images in the figure shows snapshots of a palladium (Pd) surface with single water molecules appearing as bright spots. In this sequence the diffusing molecule forms a rapidly moving dimer, then a trimer, a tetramer and finally an immobile pentamer.

The trajectory of a single water molecule on a Pd(111) surface at 52.4 K is also shown. The water molecules resides on top of Pd atoms, as shown by comparing images resolving the Pd atomic lattice with images resolving the water molecules.

The surprisingly fast diffusion of small clusters relative to single molecules (more than 4 orders of magnitude faster for dimers) is proposed to be a result of the stronger H-bonding between the molecules, than with the Pd substrate. This H-bonding is thought to alter the relative position of the individual water molecules in the cluster, which then might no longer match that of the substrate. The mismatch would cause the cluster to "slide" easily on the surface since not all the water molecules would be on favorable adsorption sites simultaneously. This phenomenon is thought also to be a key ingredient in the superlubricity of materials whose contacting surfaces are out of registry.

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T. Mitsui, M. K. Rose, E. Fomine, D. F. Ogletree, M. Salmeron, "Water Diffusion and Clustering on Pd(111)," *Science*, 297, 1850-1852, 2002.